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International application number: PCT/US04/026926

International filing date: 18 August 2004 (18.08.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/565,053
Filing date: 22 April 2004 (22.04.2004)

Date of receipt at the International Bureau: 08 October 2004 (08.10.2004)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



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APPLICATION NUMBER: 60/565,053

FILING DATE: *April 22, 2004*

RELATED PCT APPLICATION NUMBER: *PCT/US04/26926*

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Practitioner's Docket No. 100325.0253PRO

PATENT

Preliminary Classification
Proposed Class:
Subclass:

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: John Mak, Richard B. Nielsen, Thomas King Chow, Morgon Oliver, and Vincent Wai Wong

For: Additional Methods and Configurations for Acid Gas Enrichment and Sulfur Recovery

Mail Stop Provisional Patent Application
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

COVER SHEET FOR FILING PROVISIONAL APPLICATION
(37 C.F.R. § 1.51(c)(1))

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.51(c)(1)(i). The following comprises the information required by 37 C.F.R. § 1.51(c)(1):

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):

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2. The names of the inventors are (37 C.F.R. § 1.51(c)(1)(ii)):

1. John Mak
2. Richard B. Nielsen
3. Thomas King Chow
4. Morgan Oliver
5. Vincent Wai Wong

3. Residence addresses of the inventors, as numbered above (37 C.F.R. § 1.51(c)(1)(iii)):

1. 2242 Salt Air Drive
Santa Ana, CA 92705
USA
2. 18 Callender Court
Laguna Niguel, CA 92677
USA
3. 18591 Mariposa Dr.
Villa ParK, CA 92861
USA
4. 16711 Phelps Lane
Huntington Beach, CA 92649
USA
5. 1813 S. Deerhaven Dr.
Hacienda Heights, CA 91745
USA

4. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

Additional Methods and Configurations for Acid Gas Enrichment and Sulfur Recovery

5. The name, registration, customer and telephone numbers of the practitioner are (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: Martin Fessenmaier
Reg. No. 46697
Tel. 714-641-5100
Customer No. 34284

6. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):

Docket No. 100325.0253PRO

7. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

Martin Fessenmaier
611 Anton Blvd., Suite 1400
Costa Mesa, CA 92626
USA

8. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government. (37 C.F.R. § 1.51(c)(1)(viii)).

This invention was NOT made by an agency of the United States Government, or under contract with an agency of the United States Government.

9. Identification of documents accompanying this cover sheet:

A. Documents required by 37 C.F.R. § 1.51(c)(2)-(3):

Specification:	No. of pages	8
Drawings:	No. of sheets	6

10. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is \$160.00 for other than a small entity.

11. Fee payment

Fee payment in the amount of \$160.00 is being made at this time.

12. Method of fee payment

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Date:

04/22/04



Martin Fessenmaier
Registration No. 46697
Rutan & Tucker, LLP
611 Anton Blvd., Suite 1400
Costa Mesa, CA 92626
USA
714-641-5100
Customer No. 34284

ADDITIONAL METHODS AND CONFIGURATIONS FOR ACID GAS ENRICHMENT AND SULFUR RECOVERY

Field of The Invention

5 The field of the invention is gas processing and sulfur removal, especially as it relates to enrichment of an acid gas stream with high CO₂ content and a tail gas from Claus plant.

Background of The Invention

10 There are numerous sources of natural or synthesis gas known in the art, and almost all of them contain H₂S in various quantities that require at least partial desulfurization prior to further processing or release into the atmosphere. For example, natural gas, refinery gas, synthesis gas (*e.g.*, from gasification of residual oil or coke), or Fischer-Tropsch gas-to-liquids process (GTL) gases often contain H₂S in significant amounts that would interfere with downstream processes. Furthermore, the sulfur content in the tail gas from the Claus reactors typically requires treatment before releasing the tail gas to the environment.

15 If H₂S is present in large quantities, removal is commonly accomplished by absorption in an alkaline solvent, usually with an amine solvent. H₂S is later regenerated or desorbed in a regenerator in a stripper operating at a lower pressure and elevated temperature. The acid gas from the regenerator is then typically processed in a Claus plant where the H₂S is converted to elemental sulfur by sub-stoichiometric reaction with air or oxygen.

20 However, nearly all gas streams which contain H₂S also contain a significant quantity of CO₂ and when such gases are simply scrubbed with an alkaline solution, CO₂ is co-absorbed with the H₂S. This is particularly problematic where the ratio of CO₂ to H₂S in the gas stream is relatively high, as complete removal of both gases will often produce an acid gas weak in H₂S, which tends to cause various problems in the Claus plant. Among other things, the dilution effect
25 of CO₂ in such acid gases lowers the net heating value in the acid gas and reduces the residence time in the Claus furnace, rendering sulfur conversion difficult. Moreover, such acid gases typically contain significant quantities of contaminants (*e.g.*, benzene, toluene, xylene and heavy hydrocarbons) that generally must be destroyed in the Claus furnace, which is necessary for protection of the downstream Claus reactor catalysts. Unfortunately, the CO₂ dilution effect in

such acid gases tends to lower the furnace flame temperature, thereby making destruction of these contaminants difficult.

In extreme cases, where the H₂S content in the acid gas falls below 10%, a normal Claus reaction becomes impossible and additional costly processing steps must be employed to enhance the conversion process, such as with oxygen or oxygen enriched process. Additionally, the dilution effect of CO₂ will increase the size of the Claus plant as the plant size is predominantly controlled by the total volumetric flow of acid gas.

Where the acid gas is unsuitable as feed to a Claus plant, preprocessing using a selective acid gas removal process is frequently necessary. In a typical preprocessing operation, two gas streams are produced via selective absorption of H₂S from the acid gas and subsequent stripping of the rich solvent. Thus, one gas stream predominantly comprises CO₂ and ppmv levels of H₂S, that can be sent to a thermal oxidizer or incinerator, prior to being discharged to the atmosphere. The other gas stream is enriched in H₂S and is then processed in a Claus plant, which typically must use highly reactive catalysts or followed by a tail gas treatment unit to meet the high sulfur conversion requirement in compliance with today's environmental regulations.

Known processes for selective H₂S removal from high CO₂ gases include the Stretford, LOCAT, and/or Sulferox process. These processes employ complex catalyst-based chemistry to oxidize H₂S directly to sulfur. However, these units are often complex, difficult to operate, and are limited to relatively small capacity. Alternatively, various known amine based solvents capable of selectively removing H₂S can be used. For example, selective absorption processes can be based on variations of tertiary amines (e.g., those comprising formulated methyldiethanolamine (MDEA), sterically hindered tertiary amines, and other amine-organic solvent blends). Such solvents, particularly when combined with special absorber internal designs will minimize co-absorption of CO₂ (typically, such processes can concentrate the H₂S content by a factor of three to five fold). Other processes for selective H₂S removal include the use of a variety of sterically hindered tertiary amino compounds described in U.S. Pat. Nos. 4,405,580.

In still further attempts to increase selectivity of absorption, special tray configurations can be employed to reduce the contact time with CO₂ to achieve the required selectivity. These

special equipments are designed to slow down the mass transfer between amine with CO₂ relative to that with H₂S, thereby improving the selectivity process. For example, U.S. Pat. Nos. 4,278,621 and 4,297,329 and 4,678,648 describe special tray and packing designs in minimizing CO₂ contact time. Unfortunately, the use of such processes and/or devices in most cases results
5 in only marginal benefit for treating a diluted acid gas stream.

Alternatively, as described in U.S. Pat. Nos. 4,198,386 and 4,093,701, selectivity is achieved by varying gas flow-rates using a plurality of absorption columns, and splitting the absorber column into a number of absorption zones with controlled flow-rates of lean amine solvent. However, such systems are generally not effective to treat a very diluted acid gas at low
10 pressures. They are also often costly and complicated to operate. In yet further attempts to increase selectivity, H₂S absorption may be enhanced via temperature control. Generally, a reduction in absorption temperature slows the CO₂ absorption rate. However, the cost and complexity of operating a refrigeration unit renders such an option often uneconomical.

Even where selective acid gas absorption is practiced with concurrent conversion of H₂S
15 to elemental sulfur in Claus plant, the residual sulfur content in Claus plant tail gases frequently poses additional problems. Among other things, the Claus plant tail gas often contains substantial quantities of H₂S and fails to meet the overall sulfur recovery requirement and comply with emission standards. Numerous configurations are known in the art to reduce the sulfur content of such tail gas. However, most of such configurations are relatively complex and costly.

20 Therefore, and especially where a diluted acid gas feed is encountered, currently known methods and configurations are often neither suitable nor economical. Thus, there is still a need to provide improved configurations and methods for selective acid gas enrichment.

Detailed Description

The inventors generally contemplate integrated configurations and methods of selective
25 H₂S absorption and sulfur recovery from various gases comprising H₂S and CO₂, and especially from gases in which H₂S is diluted.

In one aspect, and with respect to selective H₂S absorption, contemplated configurations employ an amine solvent (*e.g.*, methyldiethanolamine based solvent or sterically hindered tertiary amines for preferential H₂S absorption), and a dilute acid gas is first contacted with the lean solvent for selective removal of H₂S, thereby producing (1) an overhead CO₂ vapor with ppm level of H₂S suitable for disposal in an incinerator, and (2) a H₂S rich solvent that is processed in a regenerator. The regenerator produces a H₂S enriched acid gas, a portion of which is contacted by a second amine contactor, preferably using lean amine from the regenerator and semi-lean amine from the third absorber, producing an overhead CO₂ vapor with ppm level of H₂S suitable for disposal in an incinerator, and a H₂S rich solvent that is recycled to the regenerator.

In an especially preferred aspect, the acid gas enrichment process is integrated with a Claus plant and a catalytic hydrogenation and quench unit, wherein the H₂S enriched acid gas from the selective absorption process is sent to the integrated Claus unit. With respect to configurations and methods for selective H₂S absorption from an acid gas comprising CO₂, the same considerations as described in our copending U.S. provisional patent application with the title "Methods and Configurations for Acid Gas Enrichment" (filed on or about 01/20/2004 (John Mak et al.), and incorporated by reference herein) apply.

In particularly contemplated integrated configurations, the tail gas from the Claus plant is passed through a catalytic hydrogenation reactor and a quench column forming a tail gas containing a dilute concentration of H₂S. The tail gas is treated in a third absorber, using lean solvent produced from the regenerator, producing an overhead CO₂ vapor with ppm level H₂S suitable for incinerator, and a H₂S rich solvent that is either used as a semi-lean solvent to the first and second amine absorber or recycled to the regenerator. Thus, it should be recognized that contemplated configurations lower the overall treating and sulfur recovery costs while minimizing emission problems. Based on various calculations, the inventors discovered that sulfur can be recovered up to 99.7% (and even higher) with significantly reduced capital and operating costs as compared to heretofore known configurations. Therefore, viewed from another perspective, the inventors contemplate an integrated three amine absorption stage enrichment

process that enriches H₂S in diluted acid gas to about 75% while achieving a high sulfur recovery.

The contemplated configurations can also be applied to the case without integration of the tail gas from the Claus unit. In this case, the same configuration of the first two absorbers applies and the diluted acid gas can be concentrated to about 75% H₂S, with the Claus unit independently located downstream of the amine units.

Figure 1 shows an exemplary integrated configuration according to the inventive subject matter. The inventors discovered that combinations of an enrichment unit and a third absorber processing the tail gas from the Claus unit can effectively achieve a 99.7% or higher sulfur recovery with significantly reduced equipment.

Here, a two-stage Claus reactor system is used to process the enriched acid gas stream 18. It should be appreciated that a conventional sulfur plant without a tail gas treatment option would typically require four-stage Claus reactors equipped with special burner design, highly reactive catalysts, and additional processing steps in order to achieve desirable BTX (benzene, toluene and xylenes) destruction and 99% sulfur recovery. In contrast, contemplated integrated tail gas absorption configurations significantly reduce overall cost when compared to conventional plants. The effluent gas from the Claus unit (stream 30), typically comprising trace quantities of sulfur oxides and unconverted H₂S, is processed in a hydrogenation and quench unit 71. The quenched hydrogenated gas is scrubbed in the third scrubber 72 using lean amine stream 32 that is supplied from the lean amine header. The tail gas absorber overhead vapor stream 33 comprising trace levels of H₂S can be routed to incinerator for disposal.

The rich amine stream 34 from the third absorber is pumped by amine pump 73 forming stream 35 which is then combined with the rich amine stream 7 from the first absorber 51, forming stream 36. The combined stream is heated in the lean/rich exchanger 55 and fed to the common regenerator as stream 8.

Alternatively, **Figure 2** shows another exemplary integrated configuration with a Claus unit. In this configuration, the semi-lean solvent 35 from the tail gas absorber 72 is re-used in the

second absorber 52 and fed to the mid section of the second absorber. With this arrangement, the total solvent circulation and regeneration duty are significantly reduced, resulting in lower capital and operating costs of the system.

Figure 3 shows yet another exemplary integrated configuration with a Claus unit. This configuration is similar to **Figure 2** with the exception that a portion of the semi-lean solvent stream 7 from the first absorber 51 is re-used as stream 74. This semi-lean solvent is cooled in a cooler 73 to about 100°F forming stream 75. This cold semi-lean solvent is routed to the lower section of the second absorber 52. This configuration further reduces the solvent circulation and regeneration duties.

In still further preferred aspects of the inventive subject matter, it should be recognized that the acid gas stream from the regenerator can be split into a first and second stream to achieve even better H₂S removal and/or improve cost effectiveness. Such configurations may include an integrated Claus plant as depicted in the exemplary configuration of **Figure 4**, or operate as acid gas removal plant without integrated Claus plant as depicted in the exemplary configuration of **Figure 5**.

With reference to **Figure 4** where the Claus plant is integrated into the acid gas removal plant, the acid gas stream 14 from the regenerator is split into two portions: Stream 14 and stream 17. Stream 14 is fed to the bottom of absorber 72 (tail gas absorber). The hydrogenated tail gas stream 31 is fed from the Claus plant hydrogenation and quench unit to the mid section of the absorber 72. It should be recognized that such split flow configuration takes advantage of the semi-lean amine stream 200 from the top section for further absorption in the lower section of the absorber 72. Alternatively, stream 31 and stream 17 can be combined and fed to the bottom of the absorber 72. Consequently, it should be appreciated that such configurations have eliminated the requirement of previously required absorber 52, resulting in significant cost savings.

Similarly, without integrated Claus plant as shown in **Figure 5**, the acid gas stream 17 in the split-flow configuration is divided into two streams, stream 90 and 91. Stream 91 can be optionally split to stream 94 and stream 93. Stream 94 can be combined with feed gas stream 1 forming stream 92 and fed to the absorber 51 while stream 93 can be optionally fed

independently to the bottom of the absorber. Recycling at least a portion of the acid gas stream to the feed gas is particularly advantageous to further enhance the H₂S content in the enriched gas stream. Moreover, it should be recognized that such configurations may be especially useful where the flow of feed gas is variable with varying H₂S content.

5 Where reduction of solvent circulation is particularly desired, configurations according to **Figure 6** may be implemented. Here, the stream 35 from the tail gas absorber bottoms pump 73 is split into two portions: Stream 101 and stream 102. The split ratio of streams 101 to 35 varies from 0.2 to 1, and it should be recognized that the exact set point depends on the circulation rate of stream 35, and the acid gas content of the feed streams to absorber 51. Such a configuration is
10 particularly effective in reducing the overall solvent circulation and hence the energy requirement by using the semi-lean solvent from the third absorber to further absorb the acid gas in the feed systems operating at a higher pressure.

 In a further modification over the configurations depicted in Figures 1-5, the enriched acid gas stream 14 from reflux drum 60 is split into two portions: Stream 17 and 18. The split
15 ratio of stream 17 to 14 varies from 0.2 to 0.8 depending on the level of enrichment required. The higher the split ratio (*i.e.*, the higher the relative flow of stream 17), more CO₂ will be rejected in absorber 51, which will further increase the degree of H₂S enrichment from reflux drum 60. Stream 17, which has the highest concentration of H₂S, is fed to the bottom of absorber 51. The
higher concentration increases the acid gas loading of the solvent, thus further reducing the
20 overall circulation requirement.

 Thus, it should be particularly appreciated that configurations according to the inventive subject matter will produce an acid gas enriched in H₂S from a lean H₂S stream, wherein the acid gas can be enriched from about 7% to about 75% H₂S. Moreover, preferred configurations allow removal of heavy hydrocarbons and BTEX components that is problematic with sulfur
25 plant operation. Still further, it should be recognized that contemplated configurations will produce a CO₂ stream with low H₂S content suitable for disposal in incinerators.

 In present integrated Claus plant configurations, two otherwise necessary stages of Claus reactors can be eliminated, which substantially reduces overall plant cost. Still further,

contemplated configurations solve the problems of low H₂S content and lower heating content in the acid gas where the acid gas is diluted. Therefore, difficulties associated with fuel gas firing for the Claus reaction and BTEX destruction are eliminated. It should be further recognized that contemplated configurations and processes may advantageously be employed with various gas plants, sulfur plants, Gas-to-Liquid conversion plants, gasification plant, enhanced oil recovery plants, and various existing facilities that are retrofitted to meet more stringent emission requirements.

Thus, specific embodiments and applications of acid gas enrichment and sulfur recovery have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the present disclosure. Moreover, in interpreting the specification, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.



Figure 3



Figure 5

